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<p>(54) Title: THERMOSETTING ACRYLIC MATERIALS OF HIGH GLASS TRANSITION TEMPERATURE</p> <p>(57) Abstract</p> <p>The invention provides novel thermosetting acrylic compositions, optical films, a process for making such films, and articles of manufacture produced therefrom. The invention is directed to the use of such an optical film as a substrate for flat panel visual displays such as liquid crystal displays. The materials have good optical properties including low birefringence for high contrast and color purity, low haze high transmission for minimal light loss to reduce power consumption and increased brightness. The films have a high degree of flatness, good gas barrier properties, chemical resistance, scratch resistance and dimensional stability. The thermosetting acrylic composition has a mixture of polymerizable acrylates including at least one multifunctional acrylic monomer, at least one multifunctional acrylic oligomer and a bimodal polymerization initiator composition comprising a mixture of either a photopolymerization initiator or a low temperature which initiators polymerization at a temperature of from about 40 °C to about 120 °C; plus a high temperature thermal polymerization initiator which initiates polymerization or cross-linking of the acrylates and pre-polymerized acrylates at a temperature of from about 180 °C or more.</p>		

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THERMOSETTING ACRYLIC MATERIALS OF HIGH GLASS TRANSITION TEMPERATURE

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CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of provisional application number 60/009,099 filed December 22, 1995 which is incorporated herein by reference.

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BACKGROUND OF THE INVENTION

The present invention relates to novel acrylic compositions, optical films produced from such compositions, a process for making such films, and articles of manufacture produced therefrom. More specifically, the invention is directed to an optical film useful as a substrate for visual flat panel displays (FPDs) such as liquid crystal displays (LCDs). Recent development of full color LCDs with multimedia capability, which demonstrate high quality and high speed display of both video image and computer data, has prompted proliferation of LCD technology into a variety of industries such as computers, communications, aerospace, automotive, transportation, and consumer products.

Due to product requirements as well as complex fabrication processes, the substrates for LCD cells must meet stringent prerequisites. Most flat panel visual displays, such as LCDs use an inorganic glass as its substrate.

However, glass suffers from a number of disadvantages. The high price of the special grade of glass that meets stringent LCD requirements as well as the inability of glass to be used in a roll-to-roll assembly line contributes to

the high cost of LCDs. Glass is also less desirable for portable LCD devices because of its fragility and weight. The fragility of glass also causes many other problems for storage and transportation. The shape of glass for LCDs is also limited due to its brittleness. Plastic substrates offer many advantages compared to glass substrates. It has thus been proposed and attempted to use transparent plastic substrates to replace glass as LCD substrates. This is desired not only because of the need for rugged display products but also because of the greater manufacturing yields it enables. In addition, the lighter weight and the thin film capability of polymeric materials are consistent with the LCD industry trend toward thinner and lighter displays. Moreover, plastic materials offer the opportunity for a continuous roll-to-roll device fabrication process which would be much more cost effective than a batch process using glass substrates.

In the prior art, various transparent thermoplastic polymers have been studied for this purpose but they are not generally useful in commercial LCDs. The use of thermoplastic plastic substrates is limited since they cannot meet all the LCD display requirements. Most suffer from low heat distortion temperature (HDT), insufficient stability, high birefringence, low surface hardness, low chemical resistance, brittleness, and/or poor optical quality. For example, U.S. patent 4,419,399 which is incorporated herein by reference, teaches away from the use of acrylic films for liquid crystal displays since they are too brittle. U.S. patent 4,456,638 which is incorporated herein by reference, discloses acrylic packaging material for a liquid crystal display, however, chemical resistance can only be achieved by applying an overcoating. This invention solves the aforementioned problems through the use of improved thermosetting acrylic compositions. This invention provides a new class acrylic materials which are useful for

producing high optical quality films which are clear, transparent materials with HDT over 210 °C, surface hardness of 3H or higher, high chemical resistance, and low birefringence. The materials are thermally stable enough to endure high temperature device fabrication processes such as coating of polyimide alignment layers and thermal cycles for final product applications in different environments. The materials possess good optical properties including low birefringence for high contrast and color purity, low haze high transmission for minimal light loss to reduce power consumption and increase brightness. The films produced with these thermoset acrylics also demonstrate high flatness, chemical resistance, scratch resistance and dimensional stability. Furthermore, the films produced from these materials can be bent without breaking around mandrels smaller than 0.5 inch in diameter and therefore are suitable for roll-to-roll processing, which will greatly reduce LCD manufacturing costs. Hence, this invention presents new thermosetting (meth)acrylate materials for applications in FPDs, especially LCDs, as substrates having excellent properties and performance that meet or exceed the key LCD industry material requirements.

BRIEF DESCRIPTION OF THE DRAWINGS

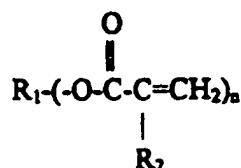
Figure 1 is a schematic representation of a color liquid crystal display.

DESCRIPTION OF THE INVENTION

The invention provides a thermosetting acrylic composition which comprises:

a) a mixture of polymerizable acrylates comprising:

- (i) at least one multifunctional acrylic monomer having the generalized formula

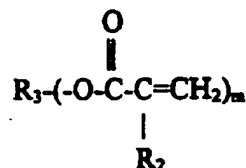


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wherein R_1 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of less than about 500; n ranges from 2 to about 6, and R_2 is H or CH_3 ;

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(ii) at least one multifunctional acrylic oligomer having the generalized formula



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wherein R_3 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of from about 500 to about 30,000; m ranges from 2 to about 10, and R_2 is H or CH_3 ;

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b) a bimodal polymerization initiator composition comprising a mixture of (i) and (ii):

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(i) at least one polymerization initiator selected from the group consisting of at least one photopolymerization initiator capable of initiating polymerization of the mixture of acrylates (a) upon exposure to sufficient actinic radiation, and at least one low temperature thermal polymerization initiator capable of initiating polymerization of the mixture of acrylates (a) at a temperature of from about 40 °C to about 120 °C;

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(ii) at least one high temperature thermal polymerization initiator capable of initiating polymerization or crosslinking of the mixture of acrylates (a), and the product of the polymerization of the mixture of

acrylates (a) with the at least one polymerization initiator (i), at a temperature of from about 180 °C or more.

5 The invention also provides a method of producing a thermoset acrylic film which comprises (I) forming the above thermosetting acrylic composition; (II) casting the thermosetting composition into a film having a substantially uniform thickness; (III) polymerizing the mixture of polymerizable acrylates with the at least one polymerization initiator (I); and (IV) further
10 polymerizing or crosslinking the result from (III) with the at least one thermal polymerization initiator (ii).

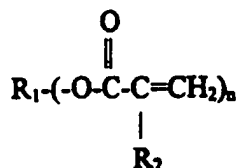
The invention further provides a thermoset acrylic film which comprises a substantially uniform layer of a polymerized and crosslinked acrylic
15 composition, which acrylic composition, prior to being polymerized and crosslinked comprises the above thermosetting composition; said film having a thickness of from about 0.05 mm to about 1.0 mm, being substantially colorless on the Gardner Yellow Color Scale according to ASTM D1544, having a optical transparency in the visible region of the electromagnetic
20 spectrum as measured by a spectrophotometer of at least about 85%, excluding reflection loss; Tg of at least about 190°C; an optical birefringence of less than about 15 nm net retardation per 100 µm of film thickness; a surface hardness as measured by ASTM D3363 of at least about 3H; a coefficient of thermal expansion of less than about 60 ppm/K; sufficient
25 chemical resistance to pass ASTM D543; sufficient flexibility to pass the 0.5 inch mandrel test of ASTM D1737; is capable of retaining optical transparency when heated at 200 °C for 1 hour; and having less than about 1% weight loss when heated at 200 °C for 1 hour.

The invention still further provides a visual display which comprises a substrate, the above thermoset acrylic film attached to the substrate, and a visual display material between the substrate and the thermoset acrylic film.

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As used herein, "multifunctional" means a compound which have more than one reaction site available for a polymerization or crosslinking reaction. The multifunctional polymerizable acrylate monomer or monomers used in this invention have the generalized formula

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wherein R_1 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of less than about 500; n ranges from 2 to about 6, and R_2 is H or CH_3 . In the preferred embodiment, R_1 comprises flexible aliphatic chains of about 10 carbon atoms or less and preferably 4 carbon atoms or less per acrylate functionality. Suitable linkage structures include methylene, ethylene, propylene, hexylene, ethylene oxide, ethoxylated bisphenol A, phenylene, etc. To ensure high resistance to thermal degradation and discoloration, thermally stable molecular structures of R_1 are preferred. Suitable linkage structures include saturated aliphatic and aromatic hydrocarbons, ethers and esters. To ensure low birefringence, R_1 linkages with low stress optic coefficient and optical polarizability are preferred. Suitable linkage structures include alkylene, alkylene oxide, etc. In the preferred embodiment, in order to ensure the most favorable high HDT and glass transition temperature (T_g), R_2 is CH_3 . Examples of suitable multifunctional acrylate monomers include, but are not limited to bifunctional monomers such as 1,4-butanediol di(meth)acrylate; butylene

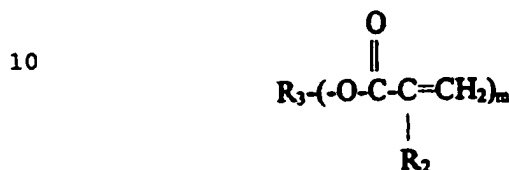
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glycol di(meth)acrylate; ethoxylated bisphenol A di(meth)acrylate; 1,6-hexanediol di(meth)acrylate; and neopentyl glycol di(meth)acrylate; trifunctional monomers such as ethoxylated trimethylolpropane tri(meth)acrylate; pentaerythritol tri(meth)acrylate; tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate; and trimethylolpropane tri(meth)acrylate; 5 tetrafunctional monomers such as di-trimethylolpropane tetra(meth)acrylate; ethoxylated pentaerythritol tetra(meth)acrylate; and pentaerythritol tetra(meth)acrylate; pentafunctional monomers such as dipentaerythritol penta(meth)acrylate and penta(meth)acrylate ester; hexafunctional 10 monomers such as hexakis(methacryloxyethoxy triphosphazene), and copolymers and mixtures thereof. Methacrylate monomers are preferred due to their higher glass transition temperature (T_g) relative to that of other acrylate monomers. Bulky monofunctional monomers that produce high-HDT polymers after polymerization such as 3,5-dimethyladamantyl 15 methacrylate and isobornyl methacrylate are also suitable as the acrylic monomer component. All of the foregoing monomers are either commercially available or may be readily produced by those skilled in the art.

20 In the preferred embodiment, the acrylate monomer is present in an amount of from about 10% to about 98%, preferably from about 50% to about 95% and most preferably from about 75% to about 95% based on the weight of the overall thermosetting acrylic composition.

25 It is known in the art that thermosetting acrylate polymers are very brittle and not suitable to fabricate large-area, free-standing thin films. As such, thermosetting acrylate thin films that are larger than 4×4 inch and meet the aforementioned criteria are unknown in the prior art. To reduce the brittleness and improve the toughness of the acrylate polymers, oligomers

were incorporated into the composition. The oligomer also increases viscosity for better film formation. Since high optical clarity is required for optical substrate applications, oligomers that provide homogeneous films are preferred. Such oligomers are covalently bonded to the acrylate network during thermal curing to prevent phase separation during prolonged use which reduces the optical clarity due to light scattering. The thermosetting acrylic composition of this invention contains at least one multifunctional acrylic oligomer having the generalized formula



wherein R_3 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of from about 500 to about 30,000; m ranges from 2 to about 10, and R_2 is H or CH_3 . The molecular weight of the oligomer preferably ranges from about 500 to about 10,000, and most preferably from about 1,000 to about 5,000. To ensure high resistance to thermal degradation and discoloration, thermally stable molecular structures of R_3 are preferred. Suitable oligomer structures include aliphatic polyether and polyester urethanes, polyethers, polyesters, poly(styrene-maleimide), etc. To ensure low birefringence, R_3 linkages with low stress optic coefficient and optical polarizability are preferred. Suitable linkage structures include alkylene, alkylene oxide, etc. Illustrative of suitable oligomers include, but are not limited to polyether urethane (meth)acrylates; polyester urethane (meth)acrylates; epoxy (meth)acrylates; novolac epoxy(meth)acrylates; polybutadiene (meth)acrylates, and resins with (meth)acrylate side groups such as (meth)acrylated styrene-maleimide copolymers. Preferred oligomers include those which are miscible with the acrylate monomers and include Craynor aliphatic urethane diacrylates available from Sartomer Company

under the trade name of "CN964" and "CN981" and polybutadiene diacrylate also from Sartomer Company under the trade name of "CN300".

In the preferred embodiment, the acrylate oligomer is present in an amount of from about 2% to about 90%, preferably from about 5% to about 50 %
5 and most preferably from about 5% to about 25% based on the weight of the overall thermosetting acrylic composition.

The acrylate materials of this invention require a dual polymerization initiator system. The first polymerization initiator comprises either a low temperature
10 thermal polymerization initiator capable of initiating polymerization of the mixture of acrylates at a temperature of from about 40 °C to about 120 °C or a photopolymerization initiator capable of initiating polymerization of the mixture of acrylates upon exposure to sufficient actinic radiation. The second polymerization initiator is a high temperature thermal polymerization
15 initiator capable of initiating polymerization or crosslinking of the mixture of acrylates, and the product of the pre-polymerization of the mixture of acrylates at a temperature of from about 180 °C or more. The "bimodal polymerization initiator composition" refers to the use of two or more initiators whereby the low temperature or photoinitiator facilitates film
20 formation at low temperature to gel or set the resin in the desired shape and with some structural integrity, while the second or high temperature thermal initiator is initiated at a higher temperature and thus permits the attainment of the film having a high glass transition temperature ("T_g"). As used herein "low temperature thermal polymerization initiators" are defined as those
25 with a one hour half-life time temperature (T_i) below about 120°C. For the low temperature thermal polymerization initiators, T_i from about 40 °C to about 120 °C is preferred and T_i from about 80°C to about 100 °C is more preferred. The "high temperature thermal polymerization initiators" are

those with T_i greater than or equal to about 120°C, T_i preferably from about 120°C to about 250 °C is preferred and T_i from about 180 °C to about 220 °C is more preferred. The half life times can be determined through spectrophotometric techniques or chemical techniques known to practitioners of the art.

Suitable low temperature thermal polymerization initiators nonexclusively include peroxides such as benzoyl peroxide (BPO), di(sec-butyl)peroxydicarbonate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxyisobutyrate, 1,1-di-(amylperoxy)-cyclohexane, alpha-cumyl peroxyneodecanoate, t-amyl peroxyneodecanoate, lauroyl peroxide, dipropylperoxydicarbonate, decanoyl peroxide, and alkyl azo compounds wherein the alkyl group contains from about 1 to about 20 carbon atoms and preferably from about 2 to about 12 carbon atoms, such as 2,2-azobis-2-methylpropionitrile, and mixtures thereof.

Suitable high temperature thermal polymerization initiators nonexclusively include cumene hydroperoxide, t-butyl cumyl peroxide, dicumyl peroxide, di-t-butyl peroxide, t-butyl hydroperoxide, di-t-butyl diperoxy-phthalate, t-amyl perbenzoate, t-butyl perbenzoate, t-butyl peroxyacetate, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, 2,5-dihydroperoxy-2,5-dimethylhexane, t-amyl hydroperoxide, ethyl-3,3-di-(t-butylperoxy)-butyrate, 2,2-di-(t-butylperoxy)-butane and 2,2-di(t-amylperoxy)propane and mixtures thereof.

The low temperature thermal polymerization initiator may be substituted by a free radical generating photoinitiator which photolytically generates free radicals. Free radical liberating photoinitiators include any compounds

which liberate free radicals on stimulation by actinic radiation. Usually the photoinitiator is a free radical generating addition polymerization initiator activated by actinic light and is preferably thermally inactive near room temperature (e.g. from about 20 °C to about 60 °C.) Preferred

5 photoinitiators nonexclusively include those described in U.S. Patent No. 4,942,112, quinoxaline compounds as described in U. S. Patent 3,765,898; the vicinal polyketaldonyl compounds in U. S. Patent 2,367,660; the alpha-carbonyls in U.S. Patents 2,367,661 and 2,367,670; the acyloin ethers in U. S. Patent 2,448,828; the triarylimidazolyl dimers in U. S. Patent

10 3,479,185; the alpha-hydrocarbon substituted aromatic acyloins in U. S. Patent 2,722,512; polynuclear quinones in U. S. Patents 2,951,758 and 3,046,127; and s-triazines in U. S. Patent 4,656,272 which are incorporated herein by reference. Suitable photoinitiators include aromatic ketones such as benzophenone, acrylated benzophenone, 2-ethylanthraquinone,

15 phenanthraquinone, 2-tert-butylanthraquinone, 1,2-benzanthraquinone, 2,3-benzanthraquinone, 2,3-dichloronaphthoquinone, benzyl dimethyl ketal and other aromatic ketones, e.g. benzoin, benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isobutyl ether and benzoin phenyl ether, methyl benzoin, ethyl benzoin and other benzoin. Preferred free radical

20 initiators are 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure 184), benzoin, benzoin ethyl ether, benzoin isopropyl ether, benzophenone, benzodimethyl ketal (Irgacure 651), α,α -diethyloxy acetophenone, α,α -dimethyloxy- α -hydroxy acetophenone (Darocur 1173), 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one (Darocur 2959), 2-methyl-1-[4-

25 methylthio)phenyl]-2-morpholino-propan-1-one (Irgacure 907), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (Irgacure 369), poly{1-[4-(1-methylvinyl)phenyl]-2-hydroxy-2-methyl-propan-1-one} (Esacure KIP), [4-(4-methylphenylthio)-phenyl]phenylmethanone (Quantacure BMS),

di-campherquinone. The most preferred photoinitiators are those which tend not to yellow upon irradiation. Selection of a photoinitiator will depend upon the processing time and/or the spectra of the ultraviolet (UV) light curing source employed. The most preferred photoinitiators include benzodimethyl
5 ketal (Irgacure 651), α,α -dimethyloxy- α -hydroxy acetophenone (Darocur 1173), 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure-184), and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one (Darocur 2959); 2-hydroxy-2-methyl-1-phenyl-1-propanone available from Ciba-Geigy under the tradename "Daracur 1178", benzophenone and mixtures thereof.

10 In the preferred embodiment, the low temperature thermal polymerization initiator or photoinitiator is present in an amount of from about .005 % to about 5%, preferably from about .02% to about 3 % and most preferably from about .05% to about .5% based on the weight of the overall
15 thermosetting acrylic composition. In the preferred embodiment, the high temperature thermal polymerization initiator is present in an amount of from about .005% to about 5%, preferably from about .02% to about 3 % and most preferably from about .05% to about .5% based on the weight of the overall thermosetting acrylic composition.

20 The thermosetting acrylic composition may optionally include one or more additives including but not limited to defoaming agents such as those available from BYK under the tradename "BYK-A500"; surfactants such as those available from BASF under the tradename "L-12"; antioxidants such as
25 phenols and more particularly hindered phenols including Irganox 1010 from Ciba-Geigy; sulfides; organoboron compounds; organophosphorous compounds; N, N'-hexamethylenebis(3,5-di-*tert*-butyl-4-hydroxycinnamamide) available from Ciba-Geigy under the tradename

“Irganox 1098”; photostabilizers and more particularly hindered amine light stabilizers including but not limited to poly[(6-morpholino-s-triazine-2,4-diyl)[2,2,6,6-tetramethyl-4-piperidyl]imino]-hexamethylene [2,2,6,6-tetramethyl-4-piperidyl]imino)] available from Cytec Industries under the tradename “Cyasorb UV3346”; resinous modifiers such as silicones and polyesters; colorants; volume expanding compounds such as the spiral monomers known as Bailey’s monomer; and dyes. These additives may be included in quantities, based upon the total weight of the acrylic composition, from about 0 % to about 6%, and preferably from about 0.1% to about 1%.

The composition of the present invention, which is in the form of a viscous liquid solution, may be made by mixing the acrylate monomer(s), the acrylate oligomer(s), and any optional additives, preferably in the absence of solvent, under conditions of ambient pressure and a temperature of from about 25 °C to about 100 °C, and preferably from about 40 °C to about 80 °C using conventional mixing apparatus known in the art, i.e. mechanical stirrer or shakers, for about 10 minutes to about 4 hours, and preferably from about 10 minutes to about 1 hour or until the mixture is visually uniform. Then, after reducing the temperature in the mixture to less than or equal to about 60 °C, and preferably less than or equal to about 40 °C if employing a low temperature thermal initiator, or to less than or equal to about 100 °C, and preferably less than or equal to about 80 °C if employing either a photoinitiator, the chosen initiators are added thereto, and the result is further mixed for about 10 minutes to about 10 hours, and preferably from about 10 minutes to about 2 hours or until the mixture is uniform. In a preferred embodiment, all reagents including the initiators and any optional additives may be mixed together using conventional mixing devices for about

10 minutes to about 4 hours, and preferably from about 10 minutes to about 1 hour under conditions of ambient pressure and a temperature less than or equal to about 60 °C, and preferably less than or equal to about 40 °C if using either a dual thermal initiator or a low temperature thermal initiator, or
5 a temperature of less than or equal to about 100 °C, and preferably less than or equal to about 80 °C if using a photoinitiator or a high temperature thermal initiator. In order to facilitate the mixing of the reagents and optional additives to form a uniform solution and/or to regulate the viscosity of the solution, a solvent may be mixed in with the reagents and optional
10 additives either before, during, or after the addition of the thermal initiator thereto. Suitable solvents include, but are not limited to, esters, ketones, ethers, haloalkanes having from about 1 carbon atom to about 24 carbon atoms, aromatic solvents, and mixtures thereof. The solvent may be added in an amount ranging, based upon the total weight of reagents and optional
15 additives in the composition, of from about 0% to about 80 %, and preferably from about 0 % to about 20 %.

After the reagents, optional additives, and optional solvents are mixed, the resulting composition may be formed into various articles such as films using
20 methods well known in the art including but not limited to cast molding, injection molding, direct liquid casting, reactive injection molding ("RIM"), resin transfer molding ("RTM"), and slot coating. Direct liquid casting and RIM are preferred. Continuous direct liquid casting, which is similar to polymer solution casting, is more preferred. In direct liquid casting, a liquid
25 composition is spread onto a web, then the coated web is exposed to a curing source. The webs may be comprised of, for example, aluminum, stainless steel, chromium, and the like. Further details of direct liquid casting processing may be found in, for example, 15 Encyclopedia of Polymer

Science and Engineering, 146 - 153 (2nd Ed. 1989), which is incorporated herein by reference.

Curing, which may involve one or more curing steps, may be performed via techniques known by one skilled in the art at or above atmospheric pressure and at a temperature of from about 150 °C to about 250 °C and preferably from about 180°C to about 220°C for single step curing or from about 60 °C to about 120 °C and preferably from about 80°C to about 100°C for the low temperature step(s) in multistep curing and from about 120 °C to about 250 °C and preferably from about 180°C to about 220°C for the high temperature step(s) in multistep curing. The time per step for curing may range from about 1 minute to about 2 hours and preferably from about 5 minutes to about 60 minutes, depending upon the heat source selected. Suitable curing heat sources include microwave, ultraviolet ("UV") light, laser, light, infrared, or thermal, with the thermal method being preferred. More preferably, curing may occur in a nitrogen-purged, temperature controllable thermal oven. Curing with UV light is particularly preferred when a dual initiator, and more specifically when at least one photoinitiator is used. The optional solvents may be removed from the composition either before curing such as by vacuum evaporation techniques known in the art or by evaporation during curing.

Various articles, such as substrates having a thickness of from about 0.05 mm to about .5 cm and preferably from about 0.05 mm to about 1.0 mm, suitable for use in flat panel displays including LCDs, plasma displays, field emission displays, and light emitting diodes, may be formed from the composition of the present invention. The making of such substrates is well known in the art and is described in, for example, U.S. Patent 4,526,818

which is incorporated herein by reference. These visual displays basically comprise a substrate, the thermoset acrylic film of this invention attached to the substrate, and a visual display material between the substrate and the thermoset acrylic film. Liquid crystal displays comprise a substrate, the thermoset acrylic film of this invention attached to the substrate, and a layer
5 of a liquid crystal composition constrained between the substrate and the thermoset acrylic film. Other uses for articles comprised of the composition of the present invention include solar cells, optical waveguides and windows.

10 Liquid crystal display panels are known the art as demonstrated by the teachings of U.S. patents 3,840,695; 4,528,073; 4,690,511 and 4,877,697 which are incorporated herein by reference. FIG. 1 shows a typical structure of a liquid crystal color display panel 10. It has a front transparent substrate 11 which may be produced according to this invention and a front
15 transparent electrode 13 on the inner surface thereof. It also has a back transparent substrate 12 which may also be produced according to this invention and a back transparent electrode 14 in the form of a mosaic array of dot electrodes on the inner surface thereof arranged in parallel with each other. A gasket 15 is sandwiched therebetween. A 90° twisted nematic
20 liquid crystal layer 16 is interposed between the substrates 11 and 12. The outer surface of the front transparent substrate 11 is optionally provided with a front linear polarizer 17 and the outer surface of the back substrate 12 is provided with optional back linear polarizer 18 so that the polarization axes of the polarizers 17 and 18 are parallel with each other. On the outer surface
25 of the back linear polarizer 18 is a mosaic color filter 19 with a mosaic array of red, green and blue filter elements observed from the front (top of the figure) which may be illuminated by a light source (not shown) located at the rear (bottom of the figure). In the absence of an electric field across the

liquid crystal layer 16, as the polarization plane of the polarized light passing through the back linear polarizer 18 is rotated 90° by the twisted nematic liquid crystal layer 16, the polarized light cannot pass through the front linear polarizer 17. On the other hand, when a voltage is applied between the front transparent electrode 13 and the back transparent electrode 14, the twisted texture of the liquid crystal layer 16 is temporarily broken, and as a result, the polarized light passing through the back linear polarizer 18 is not modulated by the liquid crystal layer 16 and passes through the front linear polarizer 17. In this way, by selectively driving the mosaic transparent electrode 14 facing the mosaic color filter 19, red, green and blue light can be selectively observed. In a display panel, these color lights are combined to reproduce natural colors. Other display panel arrangements are well known in the art and the film of this invention may be used as cover panels for them as well.

15

Films formed from these resins have surface hardness of at least about 3H and preferably at least about 4H, which eliminates the need for a hardcoating layer, and excellent chemical resistance because of crosslinking of the materials. However, these substrates may optionally be coated with one or more of the following coatings, for example, moisture barrier, gas and/or oxygen and/or nitrogen barrier, hard coat, adhesion promotion layer, alignment layer, indium tin oxide ("ITO") or other conductive coating, color filter, retardation layer, antireflection coating, and integral coatings.

25

The films produced according to the invention are substantially colorless on the Gardner Yellow Color Scale according to ASTM D1544, have a optical transparency in the visible region of the electromagnetic spectrum as measured by a spectrophotometer of at least about 85% and preferably at

least about 90% excluding reflection loss; have a Tg of at least about 190°C, preferably at least about 210 °C and more preferably at least about 250 °C; an optical birefringence of less than about 15 nm, preferably less than about 10 nm net retardation per 100 µm of film thickness; a surface hardness as measured by ASTM D3363 of at least about 3H, preferably at least about 6H; a coefficient of thermal expansion of less than about 60 ppm/K, preferably less than about 50 ppm/K; sufficient chemical resistance to pass ASTM D543; sufficient flexibility to pass the 0.5 inch mandrel test of ASTM D1737 so that the film can be rolled; and are capable retaining optical transparency when heated at 200 °C for 1 hour; and having less than about 1% weight loss when heated at 200 °C for 1 hour.

The following non-limiting examples serve to illustrate the invention. It will be appreciated that variations in proportions and alternatives in elements of the components of the photosensitive coating composition will be apparent to those skilled in the art and are within the scope of the present invention.

The following test methods are used in the following examples:

- 1) Optical birefringence was measured with thin films by both a Metricon PC-2000 Prism Coupler and a vertical laser apparatus.
- 2) Chemical Resistance: ASTM D543 with modifications: a film sample is placed into a given chemical such as sodium hydroxide (NaOH); hydrochloric acid (HCl); N-methyl pyrrolidinone (1-methyl-2-pyrrolidinone or "NMP"), ethyl alcohol, ethanol amine, tetraethyl ammonium hydroxide, acetone, isopropanol (IPA), acetone, and liquid crystals such as "E7" available from EM Industries, Inc. for 1 hour; chemical resistance is found when the sample's weight loss is less than 0.1% and there is no color change, transmission change or width gain;

- 3) Color: Gardner Yellow Color Scale (ASTM D1544) and ASTM D1925 (via Macbeth ColorEye 3100);
- 4) Surface hardness: ASTM D3363 Pencil Hardness test;
- 5) Dynamic Mechanical Analysis (DMA): measures Tg;
- 5 1 cm x 5 cm x 1 mm samples are placed into a Dynamic Mechanical Spectrometer 110 available from Seiko Instruments Inc., USA set in the Flexural Mode (3 point bending mode) with a frequency of 1 Hz; the samples are heated at a rate of 3 °C/minute from -20 °C to 300 °C.
- 6) Thermal Decomposition Temperature ("Td") is measured by placing 10
10 mg of film in a Perkin-Elmer TGA7 thermal gravimetric analyzer, then the temperature is increased to 600 °C at a rate of 10 °C/minute; the Tg is approximately equivalent to the temperature at which about 5% of the sample's weight is lost;
- 7) Coefficient of thermal expansion (CTE): Film disks having a 10 mm
15 diameter are placed into a Perkin-Elmer Thermal Mechanical Analyzer (TMA), then the temperature is increased at a rate of 10 °C/min. from -50°C to 300 °C;
- 8) Transparency: a 1 cm x 4 cm film sample is placed into a Varian Carey 5 spectrophotometer then scanned between wavelengths of 400 nm to 800
20 nm; The transparency is recorded as the average transmission between 400 and 800 nm wavelengths after reflection loss adjustments.
- 9) Hardness: ASTM D3363;
- 10) Bending: ASTM D1737 (radius = 0.5 inches).
- 25 Example 1: A resin mixture was prepared by mixing, based upon the total weight of the resin, 40% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348", 40% (20.0 g) trimethylolpropane trimethacrylate (TMPTMA) available from

Sartomer under the tradename "SR 350", 20% (10.0 g) craynor aliphatic urethane acrylate oligomers available from Sartomer under the tradename "CN964", under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.10 g) benzoperoxide (BPO), and 0.3% (0.15 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C, respectively to form a 4x4 in. thin film. The thickness of the film is about 100 µm. Properties are given in Table 1.

Example 2: A resin mixture was prepared by mixing, based upon the total weight of the resin, 45% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348", 45% (20.0 g) trimethylolpropane trimethacrylate (TMPTMA) available from Sartomer under the tradename "SR 350", 10% (4.4 g) craynor aliphatic urethane acrylate oligomers available from Sartomer under the tradename "CN964", under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.09 g) benzoperoxide (BPO), and 0.3% (0.13 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C,

respectively to form a 4×4 in. thin film. The thickness of the film is about 100 μ m. Properties are listed in Table 1.

5 Example 3 (Comparative): A resin mixture was prepared by mixing, based upon the total weight of the resin, 33% (10.0 g) of an acrylate terminated aromatic urethane oligomer available from Biddle Sawyer Company under the tradename "T-1600" and 67% (20.0 g) 1,6-hexanediol diacrylate (HDDA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the
10 mixture to drop to 25 °C, 0.5% (0.15 g) 2,2-azobis-2-methylpropionitrile (AIBN) based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, and subsequently thermally cured at 80°C for 2 h. The film was then annealed at 200°C for 1
15 h. The thickness of the film is about 100 μ m. Properties are listed in Table 1. Unlike the films obtained in Example 1 and 2, the color of the film obtained is yellow. This discoloration is attributed to the aromatic urethane unit from the oligomer used in Example 3, which is thermally unstable and discolors upon thermal aging. The thermal discoloration of aromatic
20 urethane polymers is known in the prior art.

Example 4 (Comparative): A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR
25 348" and 50% (20.0 g) trimethylolpropane trimethacrylate (TMPTMA) available from Sartomer under the tradename "SR 350" under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.08

g) benzoperoxide (BPO), and 0.3% (0.12 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C, respectively. No integral large film was obtained because of the brittleness of the film. This brittleness is typical for untoughened, highly crosslinked polymers. Properties are given in Table 1.

10 Example 5: A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) hexakis(methacryloxyethoxy triphosphazene) (PPZ) and 50% (20.0 g) trimethylolpropane trimethacrylate (TMPTMA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.08 g) benzoperoxide (BPO), and 0.3% (0.12 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C, respectively. Properties are given in Table 1. No integral large film was obtained. The color of the film is yellow, with a color index of 3. This color is caused by the thermal discoloration of the PPZ component.

25 Example 6: A resin mixture was prepared by mixing, based upon the total weight of the resin, 67% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348" and 33% (10.0 g) trifunctional methacrylate ester available from Sartomer under the

tradename "SR 9011" under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.06 g) benzoperoxide (BPO), and 0.3% (0.09 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C, respectively. Properties are given in Table 1.

Example 7 (Comparative): A resin mixture was prepared by mixing, based upon the total weight of the resin, 67% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348" and 33% (10.0 g) 1,6-hexanediol dimethacrylate (HDDMA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.2% (0.06 g) benzoperoxide (BPO), and 0.3% (0.09 g) cumene hydroperoxide (CHP), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 90 °C and for 60 minutes at 200°C, respectively. Property data are listed in Table 1. This example produced a film with a much lower Tg than example 4 because of the higher number of carbon atoms per functionality of the flexible molecular chains linking the acrylate groups.

Example 8: A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) ethoxylated bisphenol A dimethacrylate

(EBDMA) available from Sartomer under the tradename "SR 348", 25% (10.0 g) trimethylolpropane trimethacrylate (TMPTMA) available from Sartomer under the tradename "SR 350", 25% (10.0 g) 1,6-hexanediol dimethacrylate (HDDMA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.5% (0.20 g) 2,2-azobis-2-methylpropionitrile (AIBN), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 60 °C and for 60 minutes at 120°C, respectively. The film fragments were thermally annealed at 200°C for 1 h. Properties are listed in Table 1.

Example 9 (Comparative): A resin mixture was prepared by mixing, based upon the total weight of the resin, 57% (40.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348", 14% (10.0 g) a polyether urethane acrylate oligomer available from Sartomer under the tradename "CN 981", 29% (20.0 g) 1,6-hexanediol dimethacrylate (HDDMA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.5% (0.35 g) 2,2-azobis-2-methylpropionitrile (AIBN), based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 60 °C and for 60 minutes at 120°C, respectively. The film fragments were thermally annealed at 200°C for 1 h. Properties are listed in Table 1.

Replacement of TMPTMA monomer in Example 8 with a flexible CN 981 oligomer has yielded tougher materials and a large film with lower Tg and surface hardness,

5 **Example 10:** A resin mixture was prepared by mixing, based upon the total weight of the resin, 67% (20.0 g) ethoxylated bisphenol A dimethacrylate (EBDMA) available from Sartomer under the tradename "SR 348", 33% (10.0 g) isobornyl methacrylate (IMA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the
10 temperature of the mixture to drop to 25 °C, 1.0% (0.30 g) di-t-butyl peroxide, based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured 200°C for 1 h. Properties are listed in Table 1.

15

Example 11: A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) highly ethoxylated bisphenol A diacrylate (EBDA-10) available from Sartomer under the trade name "SR 602" and
20 50% (20.0 g) pentaerythritol tetraacrylate (PETA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.5% (0.2 g) 2,2-azobis-2-methylpropionitrile (AIBN) based upon the total weight of the
25 resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 60 °C and for 60 minutes at 120°C,

respectively. The thickness of the film obtained is about 100 μm . Property data are listed in Table 1.

Example 12: A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) tripropyleneglycol diacrylate (TPGDA) and 50% (20.0 g) pentaerythritol tetraacrylate (PETA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.5% (0.2 g) 2,2-azobis-2-methylpropionitrile (AIBN) based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 60 °C and for 60 minutes at 120°C, respectively. The thickness of the film obtained is about 100 μm . Property data are given in Table 1.

Example 13 (Comparative): A resin mixture was prepared by mixing, based upon the total weight of the resin, 50% (20.0 g) trimethylolpropane triacrylate (TMPTA) and 50% (20.0 g) pentaerythritol tetraacrylate (PETA) under ambient pressure and a temperature of 60 °C in a conventional mechanical mixer. After allowing the temperature of the mixture to drop to 25 °C, 0.5% (0.2 g) 2,2-azobis-2-methylpropionitrile (AIBN) based upon the total weight of the resin, were added thereto and mixed for 30 minutes under ambient conditions. The resulting resin mixture was spread onto glass substrates under ambient conditions, then subsequently thermally cured at two temperature stages, for 60 minutes at 60 °C and for 60 minutes at 120°C, respectively. Property data are given in Table 1. Replacement of

bifunctional, flexible monomers in example 11 and 12, EBDA-10 and TPGDA, has resulted in poor film formation due to increased brittleness caused by higher crosslinking density. The increase in crosslinking density also increase surface hardness.

5

Example 14 (Comparative): A free standing thin film of poly(methyl methacrylate), available from Aldrich Chemical Company, was prepared by solution casting techniques known in the prior art. The film was annealed at 200°C for 1 h before being used as a reference for the thermosetting acrylate polymers provided in this invention. The measured properties are given in Table 1. Compared with the highly crosslinked thermosetting acrylate polymers, the linear poly(methyl methacrylate) suffers from low T_g, poor dimensional stability (large CTE), poor chemical resistance and low surface hardness, which are intrinsic problems for most thermoplastic polymers.

10

Table I. Properties of example acrylate materials

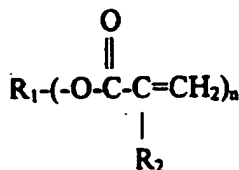
Example	T _g (°C)	T _d (°C)	CTE (ppm/K)	Film size (in.)	Color index	Retardation (nm)	Bending (0.5 in.)	Chemical resistance	Hard- ness Pencil
1	263	366	56	4x4	1	9.1	pass	pass	4H
2	>270	415	60	4x4	1	2.1	pass	pass	>9H
3	-	-	-	-	6	-	-	-	-
4	>270	331	50	<0.5x0.5	1	2.1	-	pass	>9H
5	>270	-	-	<0.5x0.5	3	1.8	-	pass	-
6	127	-	-	<1x1	1	-	-	pass	-
7	97	376	-	<1x1	1	-	-	pass	-
8	176	403	70	<0.5x0.5	1	-	-	-	2H
9	41	395	61	4x4	1	-	pass	pass	-
10	106	-	-	1x1	1	-	pass	-	-
11	40	396	74	4x4	1	-	pass	pass	HB
12	70	401	88	4x4	1	-	pass	pass	B
13	-	410	78	<0.1x0.1	1	-	-	pass	3H
14	105	354	76	-	1	-	-	fail	-

What is claimed is:

1. A thermosetting acrylic composition which comprises:

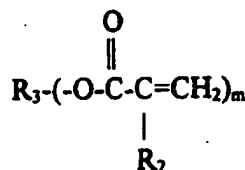
a) a mixture of polymerizable acrylates comprising:

(i) at least one multifunctional acrylic monomer having the
generalized formula



wherein R_1 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of less than about 500; n ranges from 2 to about 6, and R_2 is H or CH_3 ;

(ii) at least one multifunctional acrylic oligomer having the generalized formula



wherein R_3 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of from about 500 to about 30,000; m ranges from 2 to about 10, and R_2 is H or CH_3 ;

b) a bimodal polymerization initiator composition comprising a mixture of (i) and (ii):

(i) at least one polymerization initiator selected from the group consisting of at least one photopolymerization initiator capable of initiating polymerization of the mixture of acrylates (a) upon exposure to sufficient actinic radiation, and at least one low

temperature thermal polymerization initiator capable of initiating polymerization of the mixture of acrylates (a) at a temperature of from about 40 °C to about 120 °C;

- 5 (ii) at least one high temperature thermal polymerization initiator capable of initiating polymerization or crosslinking of the mixture of acrylates (a), and the product of the polymerization of the mixture of acrylates (a) with the at least one polymerization initiator (i), at a temperature of from about 180 °C or more.

- 10 2. The thermosetting acrylic composition of claim 1 wherein R_1 is selected from the group consisting of methylene, ethylene, propylene, hexylene, ethylene oxide, ethoxylated bisphenol A, phenylene, saturated aliphatic and aromatic hydrocarbons, ethers and esters.
- 15 3. The thermosetting acrylic composition of claim 1 wherein the multifunctional acrylic monomer is selected from the group consisting of 1,4-butanediol di(meth)acrylate; butylene glycol di(meth)acrylate; ethoxylated bisphenol A di(meth)acrylate; 1,6-hexanediol di(meth)acrylate; and neopentyl glycol di(meth)acrylate; ethoxylated trimethylolpropane
- 20 tri(meth)acrylate; pentaerythritol tri(meth)acrylate; tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate; trimethylolpropane tri(meth)acrylate; di-trimethylolpropane tetra(meth)acrylate; ethoxylated pentaerythritol tetra(meth)acrylate; pentaerythritol tetra(meth)acrylate; dipentaerythritol penta(meth)acrylate and penta(meth)acrylate ester;
- 25 hexakis(methacryloxyethoxy triphosphazene), 3,5-dimethyladamantyl methacrylate, isobornyl methacrylate and mixtures thereof.

4. The thermosetting acrylic composition of claim 1 wherein the high temperature thermal initiator is selected from the group consisting of cumene hydroperoxide, t-butyl cumyl peroxide, dicumyl peroxide, di-t-butyl peroxide, t-butyl hydroperoxide, di-t-butyl diperoxy-phthalate, t-amyl perbenzoate, t-butyl perbenzoate, t-butyl peroxyacetate, 2,5-dimethyl-2,5-di-
 5 (t-butylperoxy)hexane, 2,5-dihydroperoxy-2,5-dimethylhexane, t-amyl hydroperoxide, ethyl-3,3-di-(t-butylperoxy)-butyrate, 2,2-di-(t-butylperoxy)-butane, 2,2-di(t-amylperoxy)propane and mixtures thereof.

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5. A method of producing a thermoset acrylic film which comprises:

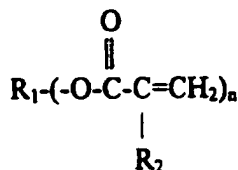
(I) forming a thermosetting acrylic composition which comprises:

a) a mixture of polymerizable acrylates comprising:

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(i) at least one multifunctional acrylic monomer having the generalized formula

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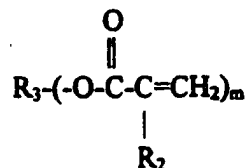


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wherein R_1 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of less than about 500; n ranges from 2 to about 6, and R_2 is H or CH_3 ;

(ii) at least one multifunctional acrylic oligomer having the generalized formula

30



wherein R_3 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of from about 500 to about 30,000; m ranges from 2 to about 10, and R_2 is H or CH_3 ;

b) a bimodal polymerization initiator composition comprising a mixture of (i) and (ii):

(i) at least one polymerization initiator selected from the group consisting of at least one photopolymerization initiator capable of initiating polymerization of the mixture of acrylates (a) upon exposure to sufficient actinic radiation, and at least one low temperature thermal polymerization initiator capable of initiating polymerization of the mixture of acrylates (a) at a temperature of from about 40 °C to about 120 °C;

(ii) at least one high temperature thermal polymerization initiator capable of initiating polymerization or crosslinking of the mixture of acrylates (a), and the product of the polymerization of the mixture of acrylates (a) with the at least one polymerization initiator (i), at a temperature of from about 180 °C or more;

(II) casting the thermosetting composition into a film having a substantially uniform thickness;

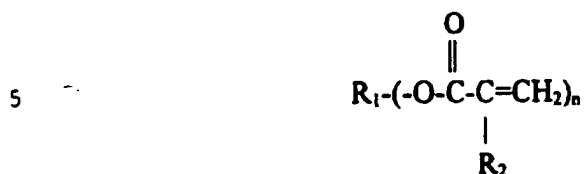
(III) polymerizing the mixture of polymerizable acrylates with the at least one polymerization initiator (i);

(IV) further polymerizing or crosslinking the result from (III) with the at least one thermal polymerization initiator (ii).

6. A thermoset acrylic film which comprises a substantially uniform layer of a polymerized and crosslinked acrylic composition, which acrylic composition, prior to being polymerized and crosslinked comprises:

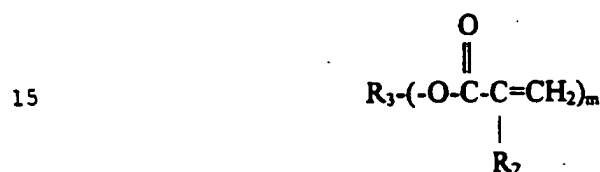
a) a mixture of polymerizable acrylates comprising:

(i) at least one multifunctional acrylic monomer having the generalized formula



wherein R_1 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of less than about 500; n ranges from 2 to about 6, and R_2 is H or CH_3 ;

(ii) at least one multifunctional acrylic oligomer having the generalized formula



wherein R_3 is an aliphatic, aromatic or mixed aromatic and aliphatic moiety having a molecular weight of from about 500 to about 30,000; m ranges from 2 to about 10, and R_2 is H or CH_3 ;

b) a bimodal polymerization initiator composition comprising a mixture of (i) and (ii):

- (i) at least one polymerization initiator selected from the group consisting of at least one photopolymerization initiator capable of initiating polymerization of the mixture of acrylates (a) upon exposure to sufficient actinic radiation, and at least one low temperature thermal polymerization initiator capable of initiating polymerization of the mixture of acrylates (a) at a temperature of from about 40 °C to about 120 °C;
- (ii) at least one high temperature thermal polymerization initiator capable of initiating polymerization or crosslinking of the mixture of

acrylates (a), and the product of the polymerization of the mixture of acrylates (a) with the at least one polymerization initiator (i), at a temperature of from about 180 °C or more;

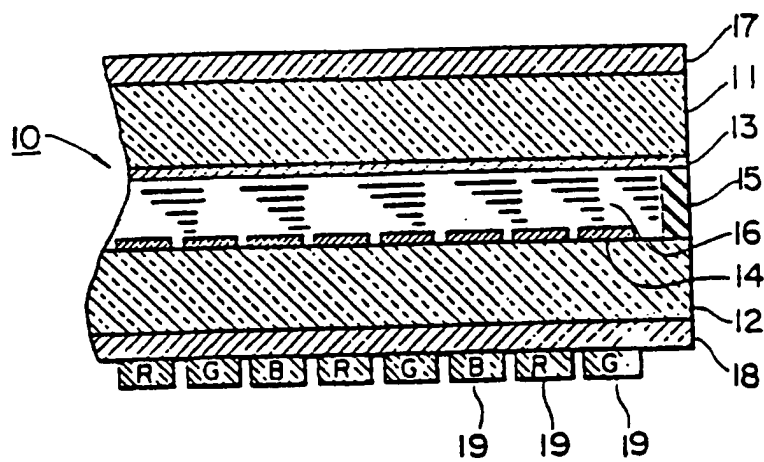
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7. A visual display which comprises a substrate, the thermoset acrylic film of claim 20 attached to the substrate, and a visual display material between the substrate and the thermoset acrylic film.

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8. A liquid crystal display which comprises a substrate, the thermoset acrylic film of claim 20 attached to the substrate, and a layer of a liquid crystal composition constrained between the substrate and the thermoset acrylic film.

FIG.1



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/20310

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F290/08 G02F1/1333

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 027 162 A (MATSUSHITA ELECTRIC IND CO LTD) 22 April 1981 see page 13, line 16-25; claims 1-4 ---	1-6
X	GB 2 089 819 A (GRACE W R & CO) 30 June 1982 see examples 3-5 ---	1-6
A	US 4 629 637 A (WALDENRATH WERNER ET AL) 16 December 1986 see the whole document ---	7,8
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 061 (C-156), 15 March 1983 & JP 57 207609 A (MATSUSHITA DENKO KK), 20 December 1982, see abstract --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

25 April 1997

Date of mailing of the international search report

23.05.97

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Internat'l Application No
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A	<p>PATENT ABSTRACTS OF JAPAN vol. 012, no. 110 (C-486), 8 April 1988 & JP 62 235310 A (JAPAN SYNTHETIC RUBBER CO LTD), 15 October 1987, see abstract -----</p>	

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